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CU-NI-MN-AL ALLOYS

This invention relates to alloys and in particular to copper based alloys containing nickel and more preferably to copper-nickel-manganese-aluminium alloys (hereinafter Cu-Ni-Mn-Al alloys).

Cu-Ni-Mn-Al alloys are widely used in marine environments where resistance to corrosion and hydrogen embrittlement are highly desirable. One such commercially available alloy known as Marinel (registered trade mark) 220 contains 19% nickel, 1.8% aluminium and 5% manganese. This alloy has a 0.2% proof stress of 700 N/mm2, UTS (ultimate tensile strength) of 870 N/mm2, elongation of 15% and a hardness of 269 BHN.

For applications where high strength and wear are especially desirable, for example bearing applications in the aerospace industry, beryllium-copper alloys having a hardness exceeding 300 BHN are currently preferred to Cu-Ni-Mn-Al alloys. However, such beryllium-copper alloys possess a low ductility (elongation of about 3%) making them susceptible to fracture under high load in an unpredictable manner. This is undesirable for many applications where failure can have catastrophic results. Moreover, beryllium is highly toxic and a Cu-Ni-Mn-Al alloy having comparable properties to existing beryllium-copper alloys would be highly desirable.

Cu-Ni-Mn-Al alloys are environmentally friendly and it would be desirable to provide a Cu-Ni-Mn-Al alloy that combines high strength with an acceptable ductility such that fracture under high load can occur in a more predictable manner allowing potential failure to be identified by routine inspection before it occurs.

A method of producing a hardened copper base alloy containing from 10 to 30% (preferably 10 to 20%) nickel and from 1 to 5% aluminium with a balance, apart from impurities, of copper is disclosed in GB 1520721. Reference is made to the addition of other elements but no specific examples of alloys or their properties are given.

We have now found that a Cu-Ni-Mn-Al alloy can be obtained having improved properties capable of wider application in which the alloy contains more than 20% nickel and the ratio of nickel to aluminium in the alloy is carefully controlled within specific limits. In particular, we have found that a Cu-Ni-Mn-Al alloy can be produced that can be used for bearing applications where high strength and high hardness which result in resistance to wear are especially desirable.

The above aims and objections are broadly achieved by the provision of a Cu-Ni-Mn-Al alloy containing nickel in the range $\geq$ 21% to $\leq$ 26% by weight, aluminium in the range $\geq$ 2.1% to $\leq$ 3.2% by weight wherein the Ni:Al ratio is at least 6.5 and preferably is between 8 and 10 (in terms of wt %), more preferably between 9 and 10 and most preferably between 9 and 9.5

Cu-Ni-Mn-Al alloys according to the present invention have improved properties compared to existing Cu-Ni-Mn-Al alloys such as Marinel 220 that makes them particularly suitable for use place of beryllium-copper alloys in applications where high strength and hardness are required.

More especially, the Cu-Ni-Mn-Al alloys according to the present invention have increased strength and hardness compared to existing Cu-Ni-Mn-Al alloys such as Marinel 220, enabling the Cu-Ni-Mn-Al alloys of the present invention to be used in place of beryllium-copper alloys.

Furthermore, the increase in strength and hardness is accompanied by only a small reduction in ductility (elongation) with the result that the Cu-Ni-Mn-Al alloys of the present invention are less susceptible to failure in an unpredictable manner compared to beryllium-copper alloys.

Additionally, the Cu-Ni-Mn-Al alloys of the present invention are environmentally friendly compared to beryllium-copper alloys which pose health and safety risks due to the toxicity of beryllium.

Preferably, manganese is present in an amount of from 2.8 to 4.1% by weight.

Cu-Ni-Mn-Al alloys according to the invention may beneficially include iron, chromium and niobium, preferably in a total amount of from 2 to 3.1% by weight, and may also optionally include one or more of titanium, vanadium, silicon, tantalum or tungsten.

The strength of the invented Cu-Ni-Mn-Al alloys is understood to derive from the precipitation of nanometre-scale Ni_3Al (γ') phases. By employing a Ni:Al ratio of at least 6.5 in terms of wt%, the formation Ni_3Al can proceed to completion leaving a proportion of nickel in solution in the copper matrix to effect solid solution hardening. We have found that a Ni:Al ratio of 8 to 10, preferably 8.5 to 9.5 and more preferably 9 to 9.5 produces an alloy with a particularly beneficial combination of strength, hardness and ductility.

Crystallographic measurements of the lattice parameters of Ni_3Al with the addition of various elements show that elements such as silicon and

vanadium decrease the lattice constant and the elements iron, chromium, manganese, titanium, tantalum and tungsten increase the lattice constant.

Such changes in the lattice parameters produce the result that silicon and vanadium increase the strengthening effectiveness of Ni_3Al through coherency hardening and iron, chromium, manganese, titanium, tantalum and tungsten increase the strengthening effectiveness of Ni_3Al through order hardening.

Of all these elements, iron, chromium, manganese are the most effective in assisting the hardening properties of Ni_3Al.

The invented Cu-Ni-Mn-Al alloys may have the composition given in Table 1.

Table 1

	% by weight
Nickel	21.0 - 26.0
Aluminium	2.1 - 3.2
Manganese	2.8 - 4.1
Iron	0.4 - 1.5
Chromium	0.3 - 1.5
Niobium	0.7 - 1.2
Titanium	0.0 - 0.5
Tungsten	0.0 - 0.5
Tantalum	0.0 - 0.5
Silicon	0.0 - 0.5
Vanadium	0.0 - 0.5
Copper	Remainder

Especially preferred alloys have the composition given in Table 2.

Table 2

	% by weight
Nickel	21.5 - 24.0
Aluminium	2.2 - 2.5
Manganese	3.0 - 4.1
Iron	0.4 - 1.1
Chromium	0.3 - 1.4
Niobium	0.7 - 1.2
Copper	Remainder

The following properties can be achieved when alloys according to the invention are subjected to thermomechanical processing (forging and/or hot rolling) in the temperature range 800°C to 1000°C followed by heat treatment in the temperature range 350°C to 600°C:

Property	**Minimum value**
0.2% Proof stress (N/mm^2)	≥ 850
Tensile Strength (N/mm^2)	≥ 1000
Elongation ($5.65\sqrt{S_0}$)	≥ 8%
Hardness (BHN)	≥ 280

Preferably the 0.2% proof stress is ≥ 850 (N/mm^2) and the hardness is ≥ 300 BHN.

The invention will now be described in more detail with reference to the following examples.

EXAMPLE 1

Experimental melt compositions for Cu-Ni-Mn-Al alloys were prepared by conventional methods having the range of compositions given in Table 3 (all amounts being % by weight)

Table 3

Melt	Ni	Al	Mn	Fe	Cr	Nb	Si	Ti	Cu	Ni:Al	Fe+Cr+Nb
AA	23.4	2.0	5.4	1.0	0.5	0.8	0.02	-	Balance	11.70	2.3
AB	25.3	2.0	5.2	1.1	0.4	0.8	0.02	-	Balance	12.65	2.3
BA	21.2	2.3	4.1	1.2	0.5	0.8	0.03	-	Balance	9.20	2.5
BB	21.5	2.5	4.0	1.1	0.4	0.7	0.01	-	Balance	8.60	2.2
BC	21.4	3.1	4.1	1.1	0.4	0.7	0.02	-	Balance	6.90	2.2
BD	21.8	2.4	3.9	1.3	0.7	0.8	0.02	-	Balance	9.10	2.8
BE	23.7	2.5	4.1	1.2	0.4	0.7	0.03	-	Balance	9.50	2.3
BH	23.8	2.5	4.0	1.2	0.4	0.7	0.02	-	Balance	9.50	2.3
BM	25.8	2.8	4.1	1.2	0.3	0.7	0.01	-	Balance	9.20	2.2

The properties for each of the alloys from Table 3 following a production route to 2" diameter bar, involving thermomechanical processing in the temperature range 800°C to 1000°C are given in Table 4

Table 4

Melt	0.2% Proof Stress(N/mm^2)	UTS (N/mm^2)	Elong (%)
AA	788	1010	20.4
AB	803	1024	19.8
BA	840	1013	9.5
BB	819	1004	11.9
BC	880	1043	13.1
BD	902	1059	9
BE	820	1030	16.4
BH	805	1003	9.6
BM	810	992	9

The results show that the strength of alloys in which the Ni-Al ratio exceeds 10, ie alloys AA and AB is lower and the ductility higher than alloys having a Ni:Al ratio in the range 6.5 to 10, i.e alloys BA to BM.

Heat treatment to effect further precipitation hardening was carried out in the temperature range 350°C to 600°C for each of the alloys BA to BM. The results are given in Table 5

Table 5

Melt	0.2% Proof Stress (N/mm^2)	UTS (N/mm^2)	Elong (%)	BHN
BA	890	1052	13.5	282
BB	841	1034	14.3	293
BC	884	1065	15.5	285
BD	907	1074	10.4	311
BE	873	1075	9.0	311
BH	858	1047	12.1	285
BM	848	1024	10.0	285

Comparison of the properties of various grades of Be-Cu alloys with Cu-Ni-Mn-Al alloys with a nickel content of less than 20% (Marinel 220), a Ni:Al ratio higher than 10 (alloy AA) and a Ni-Al ratio between 9 and 9.5 (alloy BD) is shown in Table 6

Table 6

Alloy Type	Marinel 220 Ni < 20%. Ni:Al > 10	AA Ni 23.4 Ni:Al 11.9	BD Ni 21.8 Ni:Al 9.2	Be-Cu AMS 4650 Minimum Properties	Be-Cu AMS4535 Minimum Properties	Be-Cu AMS4651 Minimum Properties
0.2% Proof Stress (N/mm^2)	720	788	907	966	931	1000
UTS (N/mm^2)	890	1010	1074	1138	1159	1241
Elongation (%)	15.5	20.4	10.4	3	4	3
Hardness (BHN)	269	277	311	335	323	340

The results show that the alloy BD having a composition according to the invention has a hardness of 311 BHN that is significantly higher than both Marinel 220 and alloy AA and is comparable with the hardness of the beryllium-copper alloys AMS 4650, AMS 4535 and AMS 4651.

The hardness of a material is a major contributor to its wear properties and the alloy BD would therefore be expected to possess wear properties not dissimilar to the beryllium-copper alloys.

In addition, the results show that the 0.2% proof stress and tensile strength of the alloy BD are comparable with that of the Be-Cu alloys AMS 4650, AMS 4535 and AMS 4651 while the elongation (ductility) is significantly improved.

The elongation (ductility) of a material is a major contributor to its performance under load and the alloy BD would therefore be expected to fracture in a more predictable manner than the Be-Cu alloys AMS 4650, AMS 4535 and AMS 4651 which have very low elongation (ductility).

EXAMPLE 2

Experimental melt compositions for Cu-Ni-Mn-Al alloys were prepared by conventional methods having the range of compositions given in Table 7 (all amounts being % by weight)

Table 7

Melt	Ni	Al	Mn	Fe	Cr	Nb	Si	Ti	Cu	Ni:Al	Fe+Cr+Nb
CA	22.8	2.3	2.0	0.3	1.2	0.7	0.02	-	Balance	9.9	2.2
CB	23.0	2.3	3.0	0.3	1.2	0.7	0.02	-	Balance	10.0	2.2
CC	21.5	2.2	2.8	0.5	1.1	0.7	0.02	0.07	Balance	9.8	2.3
CD	22.1	2.5	3.1	0.5	1.4	1.20	0.02	-	Balance	9.0	3.1
CE	21.9	2.4	3.0	0.4	1.4	1.2	0.02	0.07	Balance	9.1	3.0

These alloys have a higher chromium content and a lower iron content than the alloys shown in Table 3. CD and CE also have a higher niobium content and CC and CE also include titanium.

The alloys were then subjected to thermomechanical processing and heat treatment as in the previous example and the properties are given in Table 8.

Table 8

Melt	0.2% Proof Stress (N/mm²)	UTS (N/mm²)	Elong (%)	BHN
CA*	-	-	-	-
CB	867	1044	11.0	302
CC	901	1022	11.0	293
CD	972	1080	10.0	302
CE	970	1088	8.0	285

* no figures available for CA due to the alloy being unforgeable.

The results again show that the Cu-Ni-Mn-Al alloys according to the invention have increased strength and hardness compared to known Cu-Ni-Mn-Al alloys.

The 0.2% proof stress is generally relied on by engineers as providing an accurate indication of the strength of an alloy and the above examples show that the 0.2% proof stress of alloys according to the invention is significantly higher than that of existing Cu-Ni-Mn-Al alloys as demonstrated by Table 9 which compares the alloys of the invention with the known Marinel 220 alloy from Table 6

Table 9

Melt	0.2% Proof Stress (N/mm²)	UTS (N/mm²)	Elong (%)	BHN	Ni:Al	Ni	Al
CD	972	1089	10.0	302	9.0	22.1	2.5
CE	970	1088	8.0	285	9.0	21.9	2.4
BD	907	1074	10.4	311	9.1	21.8	2.4
CC	901	1022	11.0	293	9.8	21.5	2.2
BA	890	1052	13.5	282	9.2	21.2	2.3
BC	884	1065	15.5	285	6.9	21.4	3.1
BE	873	1075	9.0	311	9.5	23.7	2.5
CB	867	1044	11.0	302	10.0	23.1	2.3
BH	858	1047	12.1	285	9.5	23.8	2.5
BM	848	1024	10.0	285	9.2	25.8	2.8
BB	841	1034	14.3	293	8.6	21.5	2.6
Marinel 220	720	869	15.5	269	10.6	19.0	1.8

The results indicate that a significant improvement in properties is achieved compared to Marinel 220 with alloys possessing a Ni:Al ratio of between 9 and 10. Preferred alloys have a 0.2% proof stress of at least 900 (N/mm²). These include alloys CD, CE, BD, CC which have a nickel content of 21.5 to 22.1 and an aluminium content of 2.2 to 2.5.

In the above tables, the following test procedures were employed

0.2% proof stress	- BS EN 10002 Pt 1 2001
UTS	- BS EN 10002 Pt 1 2001
Elongation	- BS EN 10002 Pt 1 2001
Hardness	- BS EN ISO 6506-1:1999